Laser Enhanced Plating

APPLICATIONS TO GOLD PATTERNING

Robert J. von Gutfeld and Lubomyr T. Romankiw

IBM Corp., Thomas J. Watson Research Center, Yorktown Heights, N.Y., U.S.A.

Present processes for generating metallized patterns for microcircuitry involve many steps including mask fabrication. Maskless metallization of patterns at acceptable resolution would reduce the number of processing steps, add flexibility to the production scheme and facilitate repair of circuitry. Laser enhanced deposition of gold and other metals is believed to represent a significant advance in this field.

Recently, a new technique for depositing from and etching in aqueous solutions was described in which a focussed laser beam is used to define arbitrary patterns without the use of masks (1 to 5). The rate of plating or etching is much greater in the region of laser absorption than in the non-irradiated areas so that a pattern can be traced by movement of the beam relative to the cathode or, in the case of etching, the anode. Laser enhanced plating has been used with a variety of substrates to achieve gold, nickel and copper deposition rates as high as 10 μm/s for laser power densities in the range 1 to 10^3 kW/cm^2. Thin film lines as narrow as 2 μm have been generated by simple motion of the beam relative to the cathode. More complicated plated patterns have been generated with a computerized table to provide the necessary relative beam-cathode movement.

Plating Mechanisms

Using the apparatus shown in Figure 1, an extensive study of the copper/cupric ion plating system has yielded an understanding of the enhancement mechanisms, which are also believed to be fundamental to gold deposition. Special cathodes were designed to limit the irradiated plated area to that of a small spot several hundred micrometres in diameter, or approximately equal to that of the laser beam diameter (4). With the beam directed through an opening in the platinum anode onto the cathode, the plating current was measured as a function of applied overpotential, using a potentiostat in connection with a three-electrode system. It was found that the plating current increased by between 2 and 3 orders of magnitude with the laser beam incident on the cathode, compared to values obtained without laser irradiation. Enhancement was observed over the entire polarization curve extending from 0 to about 800 mV of applied overpotential relative to SCE (saturated calomel electrode). These results, in combination with earlier experiments using widely differing thermally conducting substrates, led to the following thermal model for laser enhancement of electrodeposition or etching:

(1) At low overpotentials, enhancement occurs due to an increase in the thermal kinetics of the plating process, resulting from laser energy absorption which causes a higher laser energy rate of charge transfer at the cathode

(2) At higher (more negative) potentials, in the absence of laser irradiation, the plating current becomes limited by the depletion of available ions in the plating region with nearby ions unable to diffuse towards the cathode sufficiently rapidly to replenish the supply required at the surface for faster plating (mass transport limited region). The laser beam causes strong thermal gradients in the surface region, which in turn produce intense local stirring of the electrolyte. The rapid replenishment of the metal ion concentration at the solution/cathode interface, which is due to local thermal convection, allows for a very high local deposition rate.

Types of Laser Plating

Three types of laser enhanced plating potentially applicable to improved gold deposition have been experimentally identified. The first, laser enhanced electrodeposition has been described above and requires an anode-cathode arrangement with an externally applied potential.

The two other types require no external potential and are thermally driven by the absorbed laser power. The first of these is laser enhanced electroless plating for which the deposition of nickel has been demonstrated (2, 5). In this process, charge conservation during plating is maintained via a catalyst in the plating solution. Since the performance of electroless solutions is generally quite temperature-sensitive, these solutions invariably operate well only at temperatures significantly above room temperature. Hence, in electroless plating, the effective deposition rate enhancement, that is the ratio of local plating produced by the heating effect of a laser beam compared to background plating, is very large and can approach infinity. The increase in temperature with laser irradiation locally also produces relatively high rates of plating though not up to the same levels as those obtainable with electroplating.

A third improved form of plating is a type of laser enhanced exchange plating (5). Here a local thermobattery is created between hot (laser irradiated) and cool regions of the cathode immersed in a conventional electroplating solution. The heated portion performs as the active cathode and becomes plated, with the cooler surrounding region functioning as an anode and

becoming etched, thereby maintaining overall charge conservation. The etching rate is low, however, since the etched area is generally much larger than that illuminated by the laser and acting as an effective cathode. The simultaneous occurrence of plating and etching is not generic to all electrolytes, since a shift in the rest potential of the interface towards a more positive value with increasing temperature is required. A negative shift causes etching of the heated region with plating of the cooler area.

Thermobattery deposition is similar to simple exchange plating which occurs when a less noble metal is immersed in an electrolyte containing ions of a metal of higher nobility. In this latter case thin deposits are produced, since the driving force is self-limiting. Typical exchange plating thicknesses are at most a few hundred nanometres because as the pores in the deposit, which are local anodic regions, close over through lateral deposit growth, the driving force disappears and plating stops. In contrast, laser enhanced thermobattery plating continues indefinitely as long as the ion concentration is sufficient and anode material is available for etching and dissolution. The latter condition is almost certainly met by any bulk specimen. The technique has been used to deposit gold and copper metallizations on glass substrates or on bulk specimens. On these latter, columns or needles up to several hundred micrometres in height have been deposited.

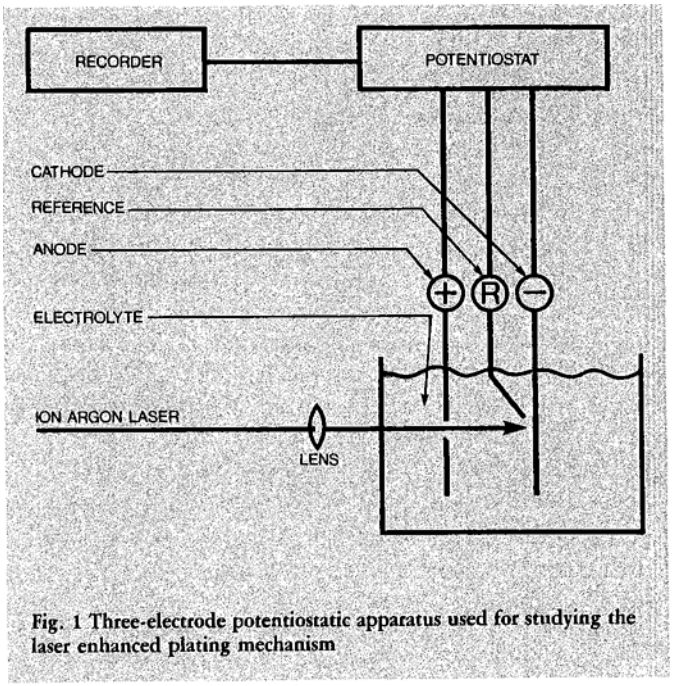

Fig. 1 Three-electrode potentiostatic apparatus used for studying the laser enhanced plating mechanism

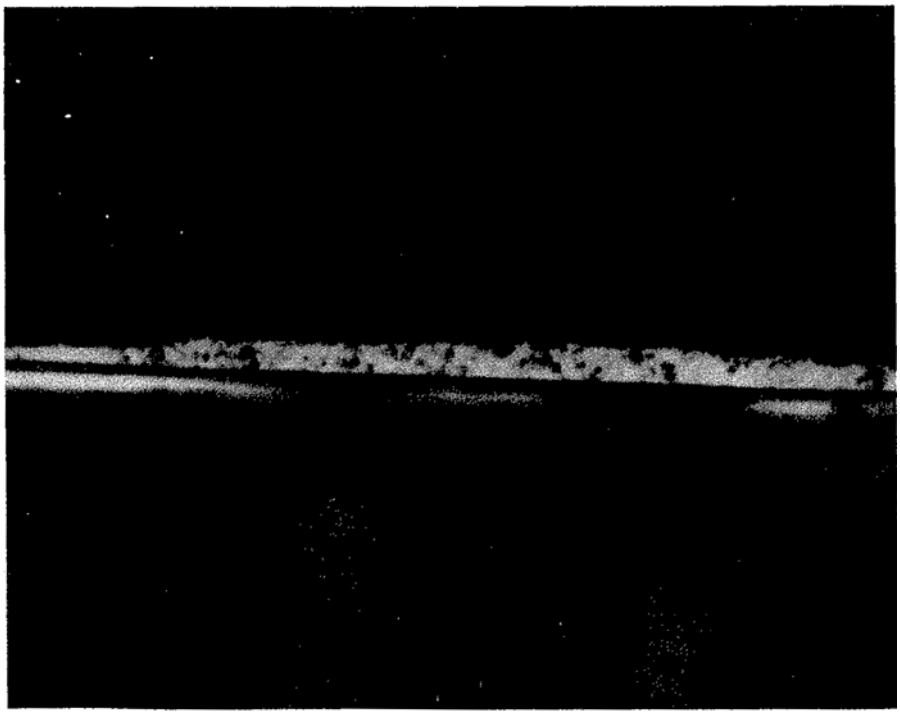

Fig. 2 Photograph of a cross-section of a laser enhanced exchange deposited gold line on nickel-plated 0.2 mm thick beryllium-copper, a material typically used for electrical contacts

Laser Enhanced Gold Plating

Although early work in laser plating concentrated on nickel and copper deposition, extensive work has been carried out recently to explore the applications of the technique to gold plating, using both electrolytic and thermobattery methods (6). Our interest lies chiefly in the use of maskless plating to localize the deposition of gold, and hence conserve it and other precious metals used in microelectronic electrical connector applications. In such applications, gold provides a good electrically conducting surface that remains corrosion-free. In many instances, high deposit hardness is required to confer wear resistance and for these, gold plating solutions containing either nickel or cobalt, which is codeposited in small amounts, are used. Substrates are generally 0.125 to 0.250 mm thick beryllium-copper, coated with 1 to 2 μm of nickel onto which the gold is deposited.

Several examples of laser enhanced gold deposition are described below to highlight the speed, utility and flexibility of this maskless plating technique. Figure 2 shows the cross-section of a linear gold deposit obtained by scanning an argon laser beam across a 0.2 mm thick nickel-plated beryllium-copper sample immersed in an exchange plating gold cyanide solution. Deposition was carried out without an external EMF, using the thermobattery mode previously described. The gold appears as a dense, uniform deposit, approximately 2 μm thick. Figure 3 shows a cross-section of an electrodeposited gold needle about 0.2 mm in height and 0.075 mm in diameter. The deposition was carried out using potentiostatic laser enhanced pulse plating. The laser on-time was synchronized with the cathode voltage pulse. A 25 per cent duty cycle was used for this, with a small anodic potential applied during the off-time. Overall the gold deposit is dense, except for small dendritic growths at the periphery of the deposit. This feature is typical of deposition in the current-limited mass transport regime and results from local ion depletion after the core was completely formed. The laser enhanced deposition rate was about 700 nm/s which compares to the usual gold electrodeposition rate of about 3 nm/s.

Figure 4 shows a gold pattern generated with the assistance of a computer driven x-y-z precision table to generate alphanumeric characters in conjunction with the laser enhanced thermobattery plating technique (no external EMF). In this example, a quartz cell which contained the sample and a exchange gold plating solution was attached to the movable table with the laser beam fixed in position. The computer was also used to control the laser power, switching it off while the table moved after the completion of one character until the start of the next. The line widths obtained are of the order of 0.15 mm, with the plating thickness approximately 200 nm. The flexibility of this laser technique suggests the additional possibility of using it to generate unique ornamental patterns of possible interest to the jewellery industry. An example of such a pattern consisting of several small non-concentric circles is shown in Figure 5.

Conclusion

Although laser enhanced deposition is still in the experimental stage, considerable progress has been made both in the understanding and in the application of the technique, especially for microelectronics. Further testing of the grain size, hardness and electrical properties of gold films laser-deposited on bulk metal samples must be carried out before the technique can be used on a production scale. Work in these areas is continuing. Other applications are under investigation, including the repair of broken gold circuit lines by local bridging with laser enhanced deposition. Success in this technique has previously been demonstrated using localized laser enhanced copper plating (4).

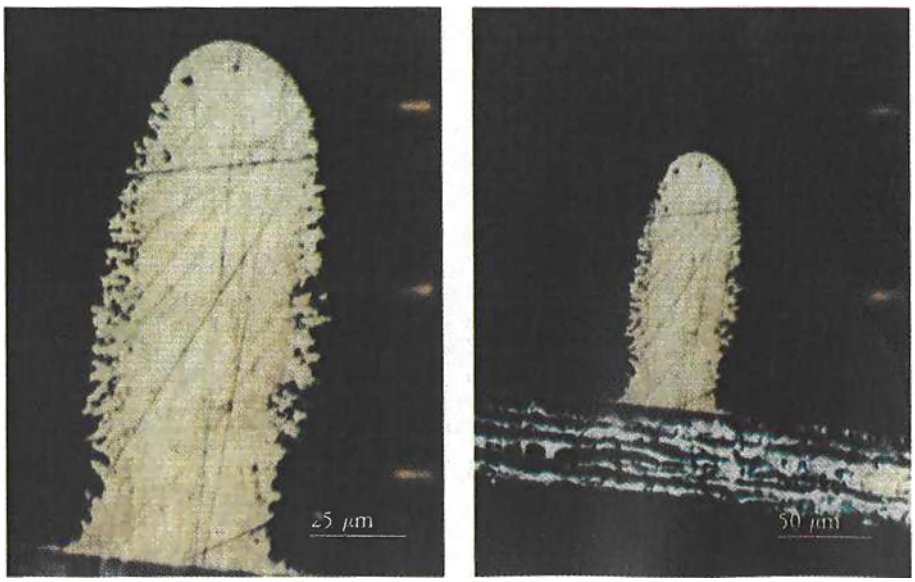

Fig. 3 Photograph of a cross-sectioned gold needle grown by laser enhanced pulse plating on a 0.075 mm thick nickel sample. Two magnifications are shown

Acknowledgements

We are grateful to Dr. M. Gelchinski for the laser enhanced electroplated and cross-sectioned samples and to Mr. D. R. Vigliotti for the computer programming used in the generation of the pattern of Figure 4. The assistance of Dr. R. Hodgson is also gratefully acknowledged.

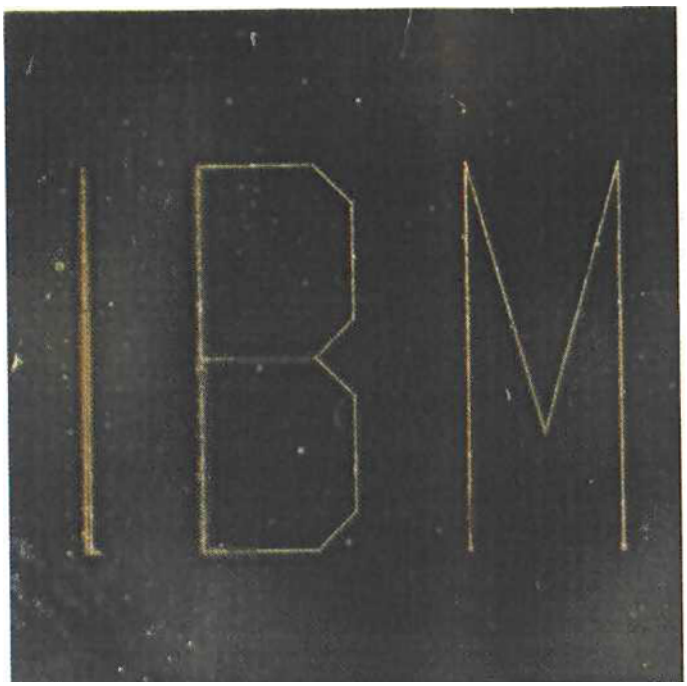

Fig. 4 Pattern generated in a gold exchange plating solution in conjunction with a computer controlled table. Characters are 10 mm high, linewidths about 0.15 mm

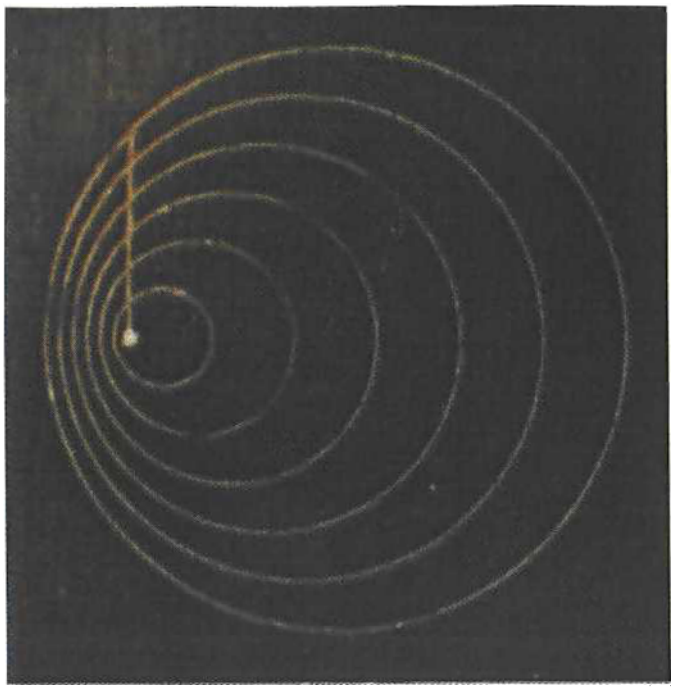

Fig. 5 Laser enhanced exchange deposited gold ornamental pattern on nickel-plated beryllium-copper substrate

References

1 R. J. von Gutfeld, E. E. Tynan, R. L. Melcher and S. E. Blum, *Appl. Phys. Lett.*, 1979, **35**, 651-653

2 R. J. von Gutfeld, E. E. Tynan and L. T. Romankiw, Abstr. 472, Electrochem. Soc. Extend. Abstr. Los Angeles, CA., 79-2, 1979, pp. 1185-1187

3 R. J. von Gutfeld and J. -Cl. Puippe, *Oberfläche-Surf*, 1981, **22**, 294-298

4 J. -Cl. Puippe, R. E. Acosta and R. J. von Gutfeld, *J. Electrochem. Soc.*, 1981, **128**, 2539-2545

5 R. J. von Gutfeld, R. E. Acosta and L. T. Romankiw, *IBM J. Res. Dev.*, 1982, **26**, (2), 136-144

6 R. J. von Gutfeld, M. Gelchinski and L. T. Romankiw, RNP 663, Electrochem. Soc., Denver, CO., *J. Electrochem. Soc.*, 1981, **128**, 448C

Gold Thin Film Formation on Liquid Surfaces

Metal atoms, where dispersed in liquids either as micro-clusters or as macroscopic particles, have found a number of applications. Clusters, sols and slurries can serve as catalysts or reactants in chemical syntheses, and noble metal sols have been employed recently in studies of the surface enhanced Raman effect, as well as of photochemical splitting of water. Some interesting results on the injection of gold atoms into water, using a simple low-pressure, fast-flow system suitable for a high vapour pressure liquid, have been reported recently (*J. Coll. Interface Sci.*, 1982, **86**, (2), 337-343) by B. L. Halpern of the Department of Chemical Engineering at Yale University. In this system gold atoms were evaporated from a wire wound around a tungsten filament and carried in a high velocity helium jet to the water surface.

Under the conditions of the experiment the most likely event would be the penetration of single gold atoms through the water surface followed by rapid growth to a stable sol within the liquid. A most striking and unexpected result reported by Halpern was the onset of thin gold island film growth on the water surface at high incident atom flux. This implies that the gold atoms have a surprisingly long surface life time prior to solvation. The films were obtained in many cases despite stirring of the water. Calculation of the characteristic life time of a gold atom on the water surface before penetration of the interface indicates that for an incident flux of $10^{17}/cm^2s$, the gold would grow to a visible film of over 100nm thickness in about 100s.

The author discusses several potential applications of this phenomenon. Among these is the possibility of producing supported catalysts by flow deposition of gold atoms, for instance, onto a stirred slurry of water and a powder such as alumina. Self-supporting metal films of submicron thickness have uses as nuclear targets, semi-transparent electrodes, and samples for fundamental thin film studies. It might be possible to evaporate gold and other films directly onto a liquid in which mobile nuclei may perhaps adjust to give, on contact, a less strained configuration with longer range order and fewer defects than are experienced with a solid substrate. Thus thin films deposited and grown on a mobile, liquid, surface may have unique properties of possible significance to the semiconductor and other fields.

C.L.